

Water-Soluble Copolymers. V. Synthesis of Low Molecular Weight Amphoteric Polyacrylamide by Foamed Copolymerization

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ABSTRACT: Amphoteric polyacrylamide of acrylamide, acryloyloxyethyl trimethylammonium chloride, sodium acrylate, and acrylic acid was synthesized by foamed copolymerization. The effects of monomer concentration and composition, initiator concentration and composition, sodium bicarbonate and stabilizer content on the polymer intrinsic viscosity and monomer conversion were examined. The monomer conversion increased with increasing initiator concentration, sodium bicarbonate and stabilizer

content. The polymer intrinsic viscosity decreased with increasing initiator concentration. The structure and low molecular weight of the amphoteric polymer were identified by fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC), respectively. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 159–164, 2010

Key words: amphoteric polyacrylamide; foamed copolymerization; low molecular weight

INTRODUCTION

Low molecular weight water-soluble polymers have extensive applications in many fields. For example, they can be used as polymer emulsifier in coating, as polymeric dispersant in papermaking, and as polymer adhesive in building etc.^{1–3} In these fields, the low molecular weight polyacrylamides are anticipated for their high effectiveness and lower price. However, the traditional polyacrylamide is prepared via aqueous solution polymerization. Its technical flow is too long and energy loss is too high. So some more effective polymerization methods have attracted great interests for the last 10 years.^{4–6}

Foamed polymerization has been found to be an alternative method for preparing water-soluble polymers⁷ although the method has been mainly used to synthesize superabsorbent polymers in the presence of crosslinking agent so far.^{8,9} Foamed polymerization has double advantages of both bulk and solution polymerization, that is, there are the characteristics of both polymerization under high monomer concentration (high purity product) and quick reaction velocity (short reaction time).⁷ The copolymer of

acrylamide and sodium acrylate was prepared by foamed polymerization using sodium carbonate as blowing agent.¹⁰ A slurry system of high monomer concentration was fully foamed with continued stirring, then the copolymerization was initiated at 15°C and the final copolymer product contained ~ 5 wt % water. As an extension of our previous work on synthesis of amphoteric polyacrylamide,¹¹ we now report a new way of obtaining low molecular weight amphoteric polyacrylamide via the foamed copolymerization, and the effects of monomer concentration and composition, initiator concentration and composition, sodium bicarbonate and stabilizer content on the polymer intrinsic viscosity and monomer conversion were discussed, as well as its structure and molecular weight were investigated, too.

EXPERIMENTAL

Materials

Monomers

Acrylamide (AM, SNF Flocculant, Taixing, China), and acryloyloxyethyl trimethylammonium chloride (DAC, Elf Atochem SA, Cedex, France) were all industrial materials, used without further purification. Sodium acrylate (NaAA, Lvcheng Chemical Manufacturer, Zhengzhou, China) had been purified from active carbon. Acrylic acid (AA) from Tianjin Chemical Reagent Co. (Tianjin, China) was analytical-grade.

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Reagents

Ammonium persulfate (APS, analytical-grade) and sodium bisulfite (SBS, analytical-grade) were chosen as free-radical redox initiators purchased from Guangzhou Chemical Manufacturer (Guangzhou, China). Sodium bicarbonate (NaHCO_3) of analytical-grade blowing agent came from Tianjin Chemical Reagent Co. (Tianjin, China). A triblock copolymer of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PF127, industrial-grade, Nanjing Weier Chemical Industry, Nanjing, China) was used as foam stabilizer. Water was doubly distilled.

Foamed copolymerization

Keeping the molar ratio of AA/NaAA at 4 : 5 (mol/mol), a mixture of 100 mL of aqueous solution containing different concentrations of AM, DAC and NaAA were first placed in a 250 mL reaction flask equipped with a magnetic stirrer. The flask was immersed in water bath at room temperature. Aqueous solutions of PF127, NaHCO_3 and APS were then put into the flask with continuous stirring. Subsequently, the aqueous solutions of SBS and AA were added with continuous stirring. When the reaction between AA and NaHCO_3 took place, immediately produced carbon dioxide bubbles, which floated to the solution surface. Foam formation and solution polymerization continued for 4–10 min under atmospheric condition, after which the bubble production ceased and the reaction mixture became a superporous white solid. The relatively dried product was taken out from the flask and cut into small pieces, further dried in a vacuum oven at 40°C until constant weight and then grinding. The polymer powder (0.1 g) showed dissolution time in water (100 mL) of less than 5 min.

For obtaining low molecular weight amphoteric polyacrylamide, the relevant factorial experimental conditions of the foamed copolymerization were designed as follows: AA/NaAA mole ratio in feed, 4 : 5 (mol/mol); mole fraction of DAC in feed, 0.10–0.30; total monomer concentration, 30–70 wt %; mole fraction of APS in redox initiator, 0.3–0.7; total initiator concentration, 0.14–0.33 wt %; NaHCO_3 concentration, 3–11 wt %; PF127 concentration, 0.1–0.8 wt %.

Identification of prepared amphoteric polyacrylamide

To identify the chemical structure of prepared amphoteric polyacrylamide, proper amounts of powder samples were mixed with predried KBr and pressed into disks. Transmission infrared spectra of the disks were recorded using a Analect RFX-65 FTIR spectrometer (Analect Instruments, Irvine).

Gel permeation chromatography (GPC) measurement

The molecular weight of amphoteric polyacrylamide was determined by GPC, which contained a Waters 410 GPC (Waters, Milford), equipped with Columns Ultrahydrogen, and a Water 410 differential refractometer. The sample was analyzed using a 0.1 M NaCl aqueous solution as an eluant, at a flow rate of 0.6 mL/min. Monodispersed polystyrene sulfonates were used as calibration standards.

Viscosity and monomer conversion measurements

The measure method of intrinsic viscosity of the amphoteric polyacrylamide was discussed in our earlier paper.¹¹ The samples of reaction system were taken out before initiating reaction and after termination reaction, respectively. The residual monomer content (X^* , equal to residual double bond) was measured by bromination titration method (1),¹² and then the molar conversion (X) of monomers was calculated (2):

$$X^*(\%) = \frac{(V_0 - V_t)W_i}{(V_0 - V_i)W_t} \times 100\% \quad (1)$$

$$X(\%) = 1 - X^*(\%) \quad (2)$$

where V_0 is the required volume of standard $\text{Na}_2\text{S}_2\text{O}_3$ solution for blank experiment, V_t is the required volume of standard $\text{Na}_2\text{S}_2\text{O}_3$ solution for sample taken from termination reaction system, W_i is the sample weight before initiating reaction, V_i is the required volume of standard $\text{Na}_2\text{S}_2\text{O}_3$ solution for sample taken from the initial mixture, W_t is the sample weight after termination reaction.

RESULTS AND DISCUSSION

Amphoteric polyacrylamide was prepared by foamed copolymerization in the presence of gas bubbles. Carbon dioxide gas was generated by the reaction of sodium bicarbonate with AA. The foam size was controlled by the amount of released gas bubbles, which was controlled by both the amount of AA and NaHCO_3 /AA system. To achieve a homogeneous gas bubble distribution in foam system, polymerization and foaming processes must occur simultaneously. So control of timing of the two processes was critical. Experimental results had shown that the NaHCO_3 /AA system used in our study provided a special trigger system that made controlling the timing less complex.⁹ However, since stabilizing a foam longer than 10 min was difficult, the gelling had to start within 10 min after the beginning of foaming. The fast gelling could be achieved by careful choices of initiator concentration and composition, monomer concentration and composition, sodium bicarbonate and stabilizer content.

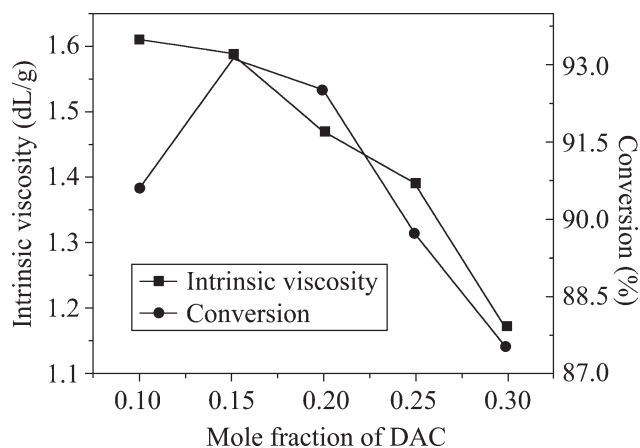


Figure 1 Effect of the mole fraction of DAC on copolymerization [conditions: monomer, 60 wt %; AA/NaAA, 4 : 5 (mol/mol); AM, 26 wt %; initiator, 0.25 wt %; APS/SBS, 1 : 1.5 (mol/mol); NaHCO₃, 4 wt %; PF127, 0.6 wt %].

Effect of (AA+NaAA)/DAC molar feed ratio

To control the chain propagation rate of polymerization and obtain water-soluble polymer, pre-neutralized NaAA was used as a copolymerized monomer.¹³ In this research, the molar ratio of AA/NaAA was fixed at 4 : 5 (mol/mol). Figure 1 shows polymeric intrinsic viscosity and monomer conversion versus mole fraction of DAC. It could be seen that the polymer intrinsic viscosity apparently decreased with an increase in the mole fraction of DAC in the monomers, which was due to the relatively lower monomer activity of DAC caused by steric hindrance, compared to AM, AA, and NaAA.^{13,14} For high mole fraction of DAC, the room temperature-initiated and self-heating copolymerization could hardly be employed, because these would result in decreased polymeric intrinsic viscosity.

In general, as seen in the above changing of polymeric intrinsic viscosity, the monomer conversion decreased with an increase in the mole fraction of DAC. However, when the mole fraction of DAC was more lower than 0.15, the system temperature increased faster than expected as long as the radical polymerization was initiated, resulting in quick breaking foam, evaporating solvent, and then the monomer crystallized, which decreased the monomer conversion.

Effect of the monomer concentration

The effect of the monomer concentration on copolymerization is shown in Figure 2.

The polymer intrinsic viscosity and monomer conversion increased with increasing total monomer concentration. This nearly is in line with the results for solution polymerization though an increase in total monomer concentration caused increases in polymerization exotherm and gelation, too. The tailing

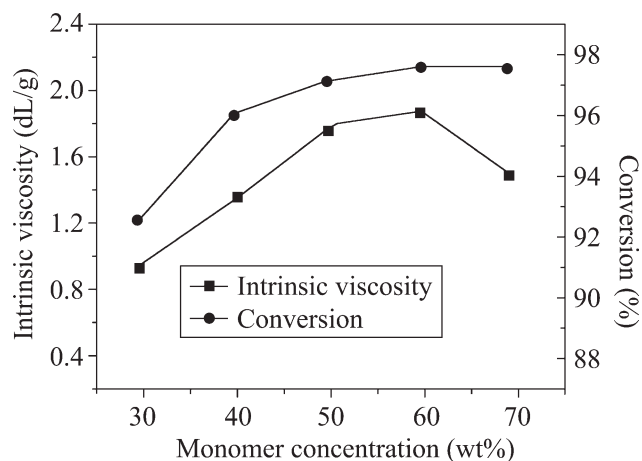


Figure 2 Effect of the monomer concentration on copolymerization [conditions: (AA+NaAA)/AM/DAC, 2 : 4 : 1 (mol/mol/mol); AA/NaAA, 4 : 5 (mol/mol); initiator, 0.25 wt %; APS/SBS, 1 : 1.5 (mol/mol); NaHCO₃, 4 wt %; PF127, 0.6 wt %].

off of intrinsic viscosity at high concentration could come from the two opposite effects: one increased in molecular weight based on the gel effect, the other decreased in molecular weight brought about by the quick exotherm. The tailing off of intrinsic viscosity was mainly due to the latter, because the higher the monomer concentration, the more conspicuous the exotherm. So the temperature dependence of termination rate and chain transfer rate constant became larger than that of propagation rate constant, which decreased the intrinsic viscosity of the copolymer.

Effect of oxidant/reductant molar ratio

Figure 3 shows polymer intrinsic viscosity and monomer conversion against mole fraction of APS.

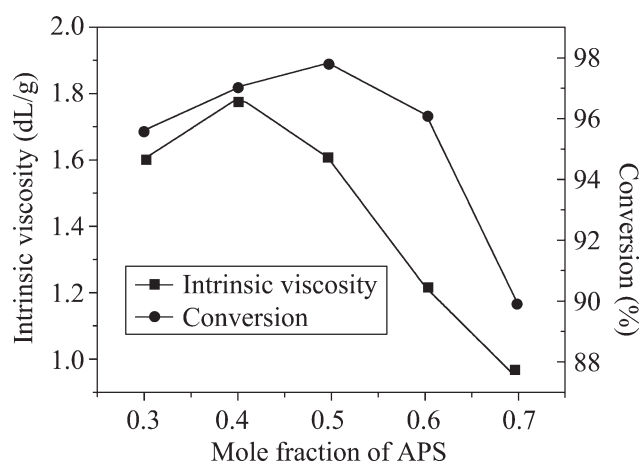


Figure 3 Effect of the mole fraction of APS on copolymerization [conditions: (AA+NaAA)/AM/DAC, 2 : 4 : 1 (mol/mol/mol); AA/NaAA, 4 : 5 (mol/mol); monomer, 60 wt %; initiator, 0.25 wt %; NaHCO₃, 5 wt %; PF127, 0.6 wt %].

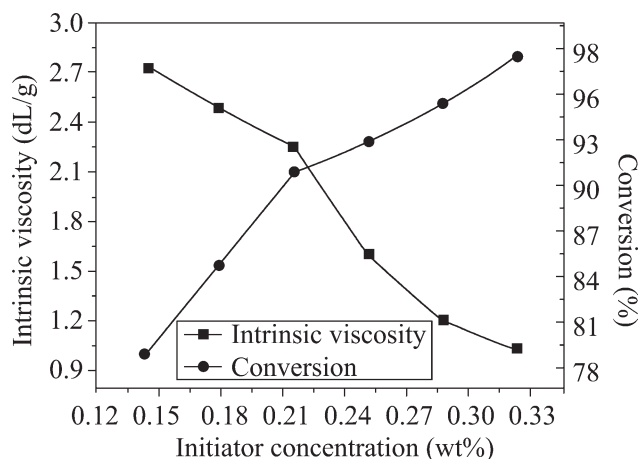


Figure 4 Effect of the initiator concentration on copolymerization [conditions: (AA+NaAA)/AM/DAC, 2 : 4 : 1 (mol/mol/mol); AA/NaAA, 4 : 5 (mol/mol); monomer, 60 wt %; APS/SBS, 1 : 1.5 (mol/mol); NaHCO₃, 5 wt %; PF127, 0.6 wt %].

The copolymers synthesized with 0.4 to 0.5 mole fraction of APS gave higher intrinsic viscosity and conversion than any other fraction range. Their dependence of the mole fraction of APS is presented by parabola shape. This is because the polymerization rate depended on the concentrations of monomers and initiator radicals in a bimolecular termination reaction. When an APS/SBS redox pair was used to initiate the free radical polymerization, the redox initiator produced two radicals,¹¹ which may be responsible for the fast polymerization. Based on the equivalent reaction mechanism between APS and SBS, the efficiency of the redox initiator was hampered with high ratio of APS/SBS as total initiator concentration was kept constant, in which the polymer molecular weight and monomer conversion became more lower than those of others.

Effect of the redox initiator concentration

A critical initiator concentration was favored at normal polymerization. Figure 4 displays the effect of the redox initiator concentration on both polymer intrinsic viscosity and monomer conversion. For a high initiator concentration, there was a sufficient amount of initiator radicals for normal polymerization to occur. Therefore, there was high monomer conversion. Likewise, the reductant (SBS) of the redox initiator could also react with free radical and deactivate the free radical or stop chain reaction under high initiator concentration,¹¹ which could decrease the polymeric molecular weight. So the polymer intrinsic viscosity decreased with increasing the initiator concentration.

Effect of sodium bicarbonate concentration

Main arena of the foam polymerization was in the liquid cell of polyhedral borders separated by the foam lamella, so the dispersion system was influenced by the amount of blowing agent. Figure 5 shows the effect of the sodium bicarbonate concentration on both polymer intrinsic viscosity and monomer conversion. The polymer intrinsic viscosity and monomer conversion increased with increasing NaHCO₃ concentration, which was due to monomer densification and aggregation effect caused from increasing the foaming extent.¹⁰ The higher NaHCO₃ concentration, the larger the foaming extent, which enhanced evaporating and carrying over small molecular as gas escaped from foam system. Monomer densification and aggregation effect made residual monomer further polymerization, and then increased polymer intrinsic viscosity and monomer conversion. However, it can be seen that the rising of the polymer intrinsic viscosity became slow when the NaHCO₃ concentration was larger than 3 wt %. During experimental design, we used an excess amount of NaHCO₃ (4–5 wt %) to make the NaHCO₃/AA trigger system work, because the simultaneously occurring processes of polymerization and foam formation could be ensured.

Effect of stabilizer concentration

The foam stabilizer PF127 used in our work was considered as it had the best foaming properties of most hydrophilic monomer systems, that was, it sustained the foam or bubbles for the longest period of time.⁹ Effect of PF127 concentration on copolymerization is shown in Figure 6. As seen in Figure 5, the

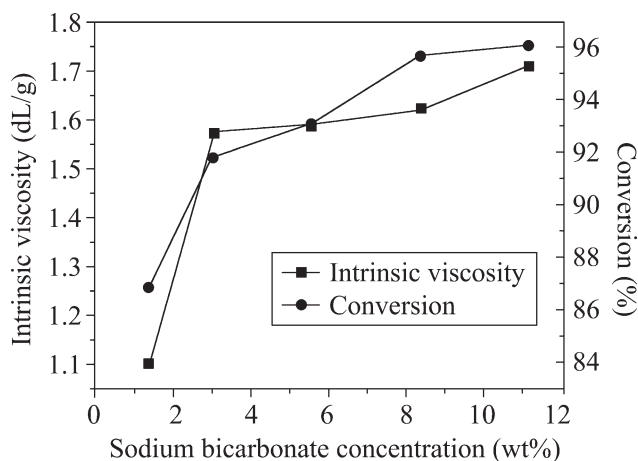


Figure 5 Effect of the sodium bicarbonate concentration on copolymerization [conditions: (AA+NaAA)/AM/DAC, 2 : 4 : 1 (mol/mol/mol); AA/NaAA, 4 : 5 (mol/mol); monomer, 60 wt %; initiator, 0.25 wt %; APS/SBS, 1 : 1.5 (mol/mol); PF127, 0.6 wt %].

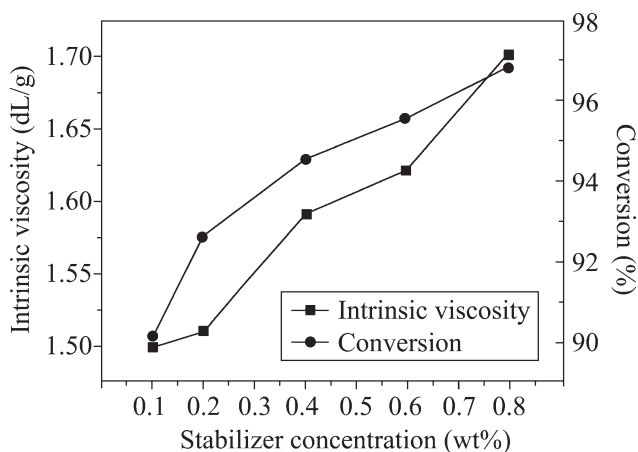


Figure 6 Effect of the foam stabilizer concentration on copolymerization [conditions: (AA+NaAA)/AM/DAC, 2 : 4 : 1 (mol/mol/mol); AA/NaAA, 4 : 5 (mol/mol); monomer, 60 wt %; initiator, 0.25 wt %; APS/SBS, 1 : 1.5 (mol/mol); NaHCO₃, 5 wt %].

polymer intrinsic viscosity and monomer conversion increased with an increasing concentration of PF127 in the solution. This was because stabilizer PF127 improved stabilization of the bubbles, which increased the foaming extent and then enhanced monomer densification and aggregation effect. In addition, the foam stabilizer PF127 was relatively polar and soluble in water and helped gel formation. So the promoted gelation prolonged the radical life and also increased the polymer molecular weight.

FTIR and GPC analyzes

Figure 7 shows a typical FTIR spectrum of the amphoteric polyacrylamide sample. A broad peak at

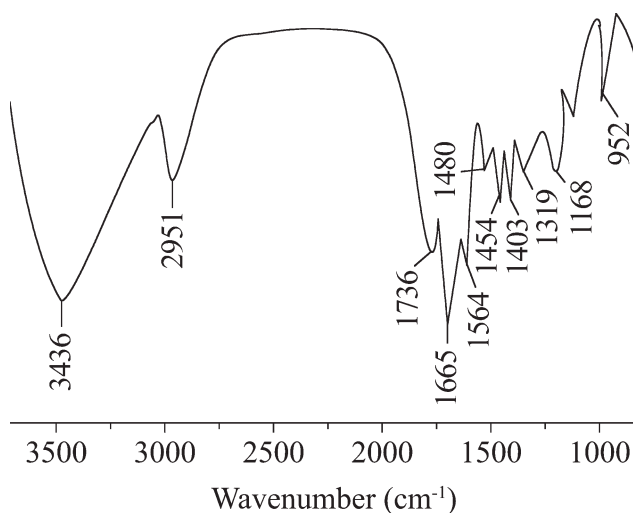


Figure 7 FTIR spectrum of (AA+NaAA)/AM/DAC amphoteric polyacrylamide. Feed ratio: (AA+NaAA)/AM/DAC, 2 : 4 : 1 (mol/mol/mol); AA/NaAA, 4 : 5 (mol/mol).

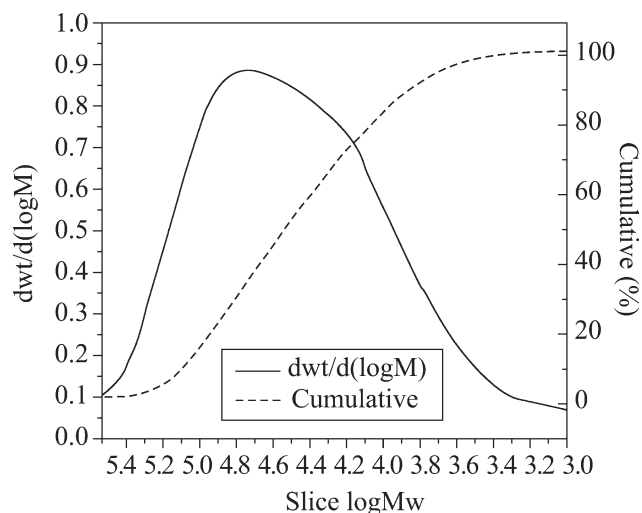


Figure 8 Molecular weight distribution of (AA+NaAA)/AM/DAC amphoteric polyacrylamide. Feed ratio: (AA+NaAA)/AM/DAC, 2 : 4 : 1 (mol/mol/mol); AA/NaAA, 4 : 5 (mol/mol).

3436 cm⁻¹ is characteristic absorbance of -COOH group, represented -AA- unit. The sharp peaks at 1319 and 1564 cm⁻¹, attributed to -COONa group in -NaAA- unit. Similarly, the sharp peak at 1665 (-CONH₂) and at 1454 [-N⁺(CH₃)₃] cm⁻¹ are characteristic absorbances of -AM- and -DAC- units, respectively. The FTIR results confirmed that the amphoteric polyacrylamide was successfully synthesized via foamed polymerization method.

For the above sample, the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the copolymer are 55,750 and 112,700, respectively. Molecular weight distribution of (AA+NaAA)/AM/DAC amphoteric polyacrylamide is displayed in Figure 8. Polydispersity index (MWD) of the sample is 2.02, which shows that the copolymer does not have excessively broad molecular weight distribution.¹⁵

CONCLUSIONS

Lower molecular weight water-soluble amphoteric polyacrylamides were successfully synthesized by foamed copolymerization of acrylamide, acryloyloxethyl trimethylammonium chloride, sodium acrylate, and AA, in the carbon dioxide foamed system stabilized by PF127 stabilizer. The main conclusions can be summarized as follows:

Polymer intrinsic viscosity can be controlled via the mole fraction of DAC, initiator concentration. Under optimum conditions, the monomer conversion was higher than 90 wt %, the range of polymer intrinsic viscosity was 1.0–3.0 dL/g, which was far smaller than 9.1–21.5 dL/g synthesized by those of a typical aqueous solution polymerization.¹¹

The chain structures of the amphoteric polyacrylamide were confirmed by the FTIR spectrum. GPC analysis indicated its properties of both lower molecular weight and better monodispersity (MWD, 2.02).

The synthetic procedure through foamed copolymerization in high monomer concentration of 60 wt % was facile and quantitative. Moreover, the foamed polymerization process was carried out very rapidly (reaction time, 4–10 min) at room temperature under atmospheric condition. So it could be considered as a good candidate to design production of low molecular weight amphoteric polyacrylamide in industrial scale.

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